

PHOTOELECTRON ASYMMETRY PARAMETERS AND BRANCHING RATIOS FOR SULFUR DIOXIDE IN THE PHOTON ENERGY RANGE 14–25 eV

D. M. P. HOLLAND

*Institute of Physical Science and Technology, University of Maryland, College Park,
MD 20742 (U.S.A.)*

A. C. PARR

*Synchrotron Ultraviolet Radiation Facility, National Bureau of Standards, Washington,
DC 20234 (U.S.A.)*

J. L. DEHMER

Argonne National Laboratory, Argonne, IL 60439 (U.S.A.)

(First received 8 April 1983; in revised form 25 June 1983)

ABSTRACT

Triply differential photoelectron spectroscopy has been performed in the photon energy range 14–25 eV for sulfur dioxide. The results are presented in the form of electronic branching ratios and asymmetry parameters, and are discussed briefly in the context of similar data for CO₂ and of the inner-shell spectra of SO₂.

As our understanding of the molecular photoionization process increases, there is a need for experimental data with which to test the various theoretical models [1]. For instance, it is important to ascertain under what circumstances the photoionization dynamics may be understood within the single-particle model, or whether a theoretical approach which explicitly includes electron correlation is required to attain proper agreement. With this objective in mind, the last few years have seen the development of sophisticated experiments which can probe the intricate and more subtle aspects of molecular photoionization. For example, triply differential photoelectron spectroscopy and fluorescence polarization spectroscopy have provided new and detailed experimental information needed to assess recent theoretical progress and to extend our understanding of molecular photoionization dynamics [2].

For molecular photoionization involving a randomly oriented target, and where the spin of the electron is not detected, only two parameters are required to describe photoionization to a particular ionic state. These are the asymmetry parameter β and the partial cross-section σ . Triply differential photoelectron spectroscopy (differential in incident photon wavelength, photoelectron kinetic energy and photoelectron ejection angle) has proved successful in measuring these parameters, and hence in providing the information required to test theory (for a recent survey of this topic, see ref. 2).

Many early studies concentrated on first-row diatomic compounds, and it is only recently that somewhat larger molecules have been investigated. Here we present electronic branching ratios and asymmetry parameters for a bent triatomic molecule, sulfur dioxide. This choice was prompted by the desire to examine a bent triatomic molecule within the framework of the extensive and very fruitful studies conducted recently for the linear triatomic molecule CO_2 [3–14]. Also, there is some evidence [15] for weak shape-resonance behavior in the sulfur $2p$ absorption spectrum of SO_2 , which may be exhibited in the valence-shell data. In fact, the present results failed to shed significant light on either original objective, and are reported here mainly as high-quality, new data, characterizing the valence-shell photoionization dynamics of SO_2 , for use as a guide in future work.

Some uncertainty has arisen concerning the precise ordering of the molecular orbitals in sulfur dioxide [16–20]. Following the analysis of the He(I) photoelectron spectrum of SO_2 by Hillier and Saunders [18] for the three outermost orbitals, and by Lloyd and Roberts [19] for the more tightly bound orbitals, the ground-state electronic configuration (C_{2v} symmetry) may be written as

$$\dots 6a_1^2 2b_1^2 7a_1^2 4b_2^2 5b_2^2 1a_2^2 8a_1^2 X^1A_1$$

The ionization potentials of the outer molecular orbitals may be given [16,18–21] as: $(8a_1)^{-1} X^2A_1 = 12.348 \text{ eV}$; $(1a_2)^{-1} A^2A_2 = 13.01 \text{ eV}$; $(5b_2)^{-1} B^2B_2 = 13.24 \text{ eV}$; $(4b_2)^{-1} C^2B_2 = 15.99 \text{ eV}$; $(7a_1)^{-1} D^2A_1 = 16.32 \text{ eV}$; $(2b_1)^{-1} E^2B_1 = 16.50 \text{ eV}$; and $(6a_1)^{-1} F^2A_1 = 20.06 \text{ eV}$. (Note that the ordering chosen agrees with the recent tabulation by Kimura et al. [20] for the outer three valence orbitals. However, the next three inner orbitals, which are not resolved experimentally, are assigned differently. Since the latter three are treated as a group in this work, we do not resolve the residual assignment problem, but have stated the above assignments for the purpose of discussion.) The similarity between several of the ionization potentials results in the appearance of three complicated bands in the photoelectron spectrum observed in the present investigation and in earlier studies. The first band consists entirely of the X^2A_1 state. Ionizations from the $1a_2$ and $5b_2$ molecular orbitals contribute to the second band, and the third band can be attributed to ionization of the $4b_2$, $7a_1$ and $2b_1$ orbitals. The

vibrational structure in all three bands is complex and has been discussed elsewhere [16, 17, 19–23]. As the resolution employed in the present experiments, ~ 110 meV, did not permit vibrational analysis, this subject will not be pursued further. The decay of various SO_2^+ states has been studied [22, 24, 25], and the photoionization yield curves [21, 26] and total cross-section [27] have been measured.

The experiments were performed using a hemispherical electron analyzer [28] coupled to a high-aperture 2 m normal-incidence monochromator [29] connected to the SURF-II storage ring at the National Bureau of Standards. The experimental technique and method of data analysis have been described previously [30]. A typical set of data is shown in Fig. 1. Under the conditions appertaining to the present experiments, the differential cross-section in the dipole approximation may be written as

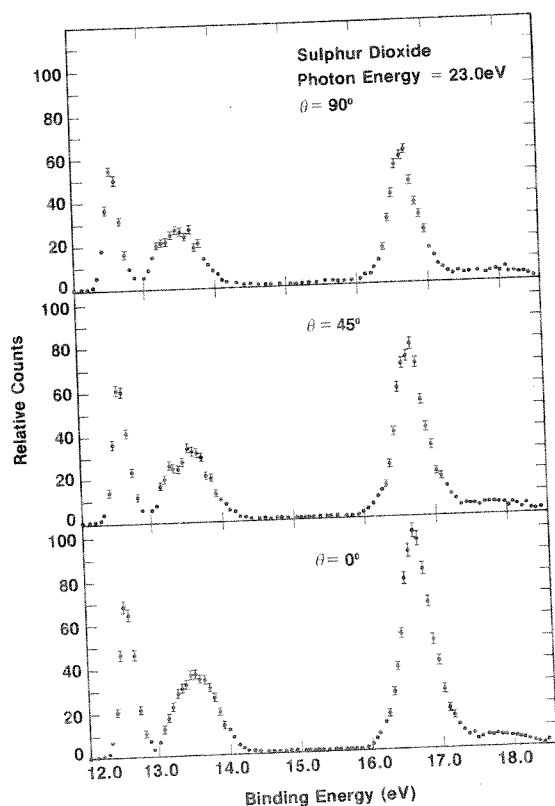


Fig. 1. Photoelectron spectra of sulfur dioxide at a photon energy of 23.0 eV and at $\theta = 0^\circ$, 45° and 90° (the spectra are normalized so that the maximum count in the $\theta = 0^\circ$ spectrum equals 100).

$$d\sigma/d\Omega = (\sigma_{\text{total}}/4\pi)[1 + (\beta/4)(3P \cos 2\theta + 1)] \quad (1)$$

where β is the photoelectron asymmetry parameter, θ the photoelectron ejection angle relative to the major polarization axis, and P the polarization of the incoming radiation. Equation (1) was used to deduce the asymmetry parameters and branching ratios presented in Figs. 2 and 3.

The spectral variations in the photoelectron asymmetry parameters for the three bands discussed above are shown in Fig. 2. The X^2A_1 asymmetry parameter (Fig. 2(a)) remains generally flat, with small fluctuations extending from close to the ionization onset up to a photon energy of ~ 22 eV. In contrast to this behavior, the β parameters for the second and third bands (Fig. 2(b) and (c)) show a generally smooth rise from threshold to reach a value of approximately unity at 25 eV. The branching ratios (Fig. 3) vary smoothly with energy, with the third band gaining intensity at the expense of the second, towards higher energies.

Sulfur dioxide possesses two more valence electrons than the linear triatomic molecule carbon dioxide. In SO_2 the two extra electrons enter the π_u orbital (in linear terminology), which is the lowest unoccupied orbital in CO_2 . In the bent form, this orbital becomes the $8a_1$ orbital and corresponds to a lone pair on the sulfur atom. Inspection [15] of the sulfur K -shell ($1a_1$) spectrum of SO_2 reveals no definite evidence of potential-barrier effects.

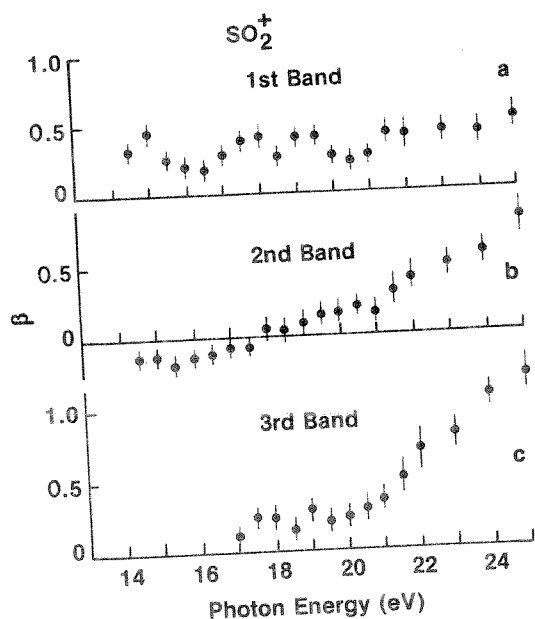


Fig. 2. Photoelectron asymmetry parameters plotted as a function of photon energy: (a) $8a_1$ orbital; (b) $(5b_2 + 1a_2)$ orbitals; (c) $(2b_1 + 7a_1 + 4b_2)$ orbitals.

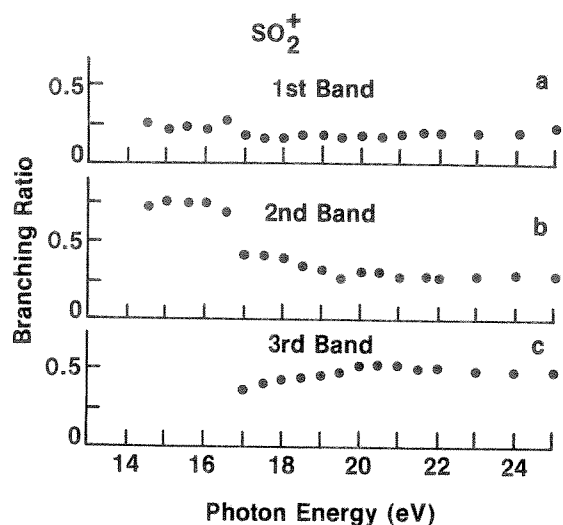


Fig. 3. Branching ratios plotted as a function of photon energy: (a) $8a_1$ orbital; (b) $(5b_2 + 1a_2)$ orbitals; (c) $(2b_1 + 7a_1 + 4b_2)$ orbitals.

This suggests that any structure observed in the X^2A_1 asymmetry parameter will not be the direct result of shape-resonance phenomena. The photoionization efficiency curves [21,26] exhibit resonant features from threshold to ~ 20 eV, which have been attributed to autoionization from Rydberg levels. Hence, it would appear that the fluctuations in the X^2A_1 β parameter are caused by autoionization from these excited states.

The $5b_2$ and the $1a_2$ orbitals correlate with π_g in a linear molecule. Theoretical work [11] has predicted and experiment has measured [8] that the asymmetry parameter for the $\text{CO}_2^+ {}^2\Pi_g$ state increases fairly smoothly from a negative value at threshold to approximately unity at a kinetic energy of ~ 30 eV. Although a shape resonance has been identified in this channel for CO_2 , it was found virtually impossible to observe it in the vibrationally averaged β curve. Hence, this vibrationally averaged β parameter was calculated under conditions pertaining to the present results for the second band of SO_2 . It is noticeable that the present data show the same overall behavior as that predicted for the $\text{CO}_2^+ {}^2\Pi_g$ state. This behavior appears to be rather common among the π orbitals of small molecules.

In contrast to the sulfur K -shell spectrum, examination of the sulfur $2p$ spectrum [15] indicates the presence of two broad peaks situated ~ 5 and 25 eV above threshold. It is conceivable that these features are the result of shape-resonance effects similar to those observed for other sulfur compounds [15]. However, even if this were the case, the peak occurring ~ 25 eV above the ionization onset would lie at too high a kinetic energy to influence the pres-

ent data. This leaves the lower-energy feature as a possible cause of resonant effects. The sulfur $2p$ electrons occupy the $2b_2$, $1b_1$ and $4a_1$ molecular orbitals, and both the second and third bands contain orbitals of the same symmetry. The β parameters for each of these bands show little, or no obvious evidence of structure which would indicate the presence of shape-resonance phenomena. A much more sensitive means for detecting resonant effects would, of course, be the measurement of vibrationally resolved asymmetry parameters and branching ratios [2]; however, this does not appear feasible at this time for SO_2 . Another observation suggesting possible shape-resonance effects is the broad peak centered at $\sim 19\text{ eV}$ found in the photoabsorption spectrum of SO_2 [27]. However, lack of theoretical guidance on this point makes it wise to defer further discussion until appropriate calculations have been performed.

ACKNOWLEDGMENTS

We wish to thank R. P. Madden for his support and encouragement throughout this work. We appreciate the valuable assistance provided by G. Rakowsky and the staff of the National Bureau of Standards' SURF-II facility. This work was supported in part by the Office of Naval Research, the U.S. Department of Energy and NATO (Grant 1939).

REFERENCES

- 1 T. N. Rescigno, B. V. McKoy and B. Schneider (Eds.), *Electron-Molecule and Photon-Molecule Collisions*, Plenum, New York, 1979.
- 2 J. L. Dehmer, D. Dill and A. C. Parr, in S. McGlynn, G. Findley and R. Huebner (Eds.), *Photophysics and Photochemistry in the Vacuum Ultraviolet*, D. Reidel, Dordrecht, Holland, 1983 (to appear).
- 3 C. E. Brion and K. H. Tan, *Chem. Phys.*, 34 (1978) 141.
- 4 T. Gustafsson, E. W. Plummer, D. E. Eastman and W. Gudat, *Phys. Rev. A*, 17 (1978) 175.
- 5 P. W. Langhoff, T. N. Rescigno, N. Padial, G. Csanak and B. V. McKoy, *J. Chim. Phys.*, 77 (1980) 589.
- 6 J. R. Swanson, D. Dill and J. L. Dehmer, *J. Phys. B*, 13 (1980) L231.
- 7 T. A. Carlson, M. O. Krause, F. A. Grimm, J. D. Allen, D. Mehaffy, P. R. Keller and J. W. Taylor, *Phys. Rev. A*, 23 (1981) 3316.
- 8 F. A. Grimm, J. D. Allen, T. A. Carlson, M. O. Krause, D. Mehaffy, P. R. Keller and J. W. Taylor, *J. Chem. Phys.*, 75 (1981) 92.
- 9 R. R. Lucchese and B. V. McKoy, *J. Phys. Chem.*, 85 (1981) 2166.
- 10 N. Padial, G. Csanak, B. V. McKoy and P. W. Langhoff, *Phys. Rev. A*, 23 (1981) 218.
- 11 J. R. Swanson, D. Dill and J. L. Dehmer, *J. Phys. B*, 14 (1981) L207.
- 12 R. R. Lucchese and B. V. McKoy, *Phys. Rev. A*, 26 (1982) 1406.
- 13 P. M. Dittman, D. Dill and J. L. Dehmer, *Chem. Phys.*, to be published.

- 14 A. C. Parr, D. L. Ederer, J. L. Dehmer and D. M. P. Holland, *J. Chem. Phys.*, 77 (1982) 111.
- 15 J. L. Dehmer, *J. Chem. Phys.*, 56 (1972) 4496.
- 16 J. H. D. Eland and C. J. Danby, *Int. J. Mass Spectrom. Ion Phys.*, 1 (1968) 111.
- 17 D. W. Turner, C. Baker, A. D. Baker and C. R. Brundle, *Molecular Photoelectron Spectroscopy*, Wiley-Interscience, London, 1970, pp. 61-131.
- 18 I. H. Hillier and V. R. Saunders, *Mol. Phys.*, 22 (1971) 193.
- 19 D. R. Lloyd and P. J. Roberts, *Mol. Phys.*, 26 (1973) 225.
- 20 K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki and S. Iwata, *Handbook of He(I) Photoelectron Spectra of Fundamental Organic Molecules*, Japan Scientific Societies Press, Tokyo, 1981, pp. 40-41.
- 21 J. Erickson and C. Y. Ng, *J. Chem. Phys.*, 75 (1981) 1650.
- 22 M. J. Weiss, T. Hsieh and G. G. Meisels, *J. Chem. Phys.*, 71 (1979) 567.
- 23 C. Y. R. Wu and C. Y. Ng, *J. Chem. Phys.*, 76 (1982) 4406.
- 24 B. Brehm, J. H. D. Eland, R. Frey and A. Küstler, *Int. J. Mass Spectrom. Ion Phys.*, 12 (1973) 197.
- 25 G. Dujardin and S. Leach, *J. Chem. Phys.*, 75 (1981) 2521.
- 26 V. H. Dibeler and S. K. Liston, *J. Chem. Phys.*, 49 (1968) 482.
- 27 C. Y. R. Wu and D. L. Judge, *J. Chem. Phys.*, 74 (1981) 3804.
- 28 A. C. Parr, R. Stockbauer, B. E. Cole, D. L. Ederer, J. L. Dehmer and J. B. West, *Nucl. Instrum. Methods*, 172 (1980) 357.
- 29 D. L. Ederer, B. E. Cole and J. B. West, *Nucl. Instrum. Methods*, 172 (1980) 185.
- 30 A. C. Parr, D. L. Ederer, J. B. West, D. M. P. Holland and J. L. Dehmer, *J. Chem. Phys.*, 76 (1982) 4349.